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(54) METHOD FOR MANUFACTURING LAMINATED SHEET

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a laminated sheet suitable as a flexible substrate material not having bad appearance such as wrinkles or the like generated at the time of thermal lamination.

SOLUTION: In a method for manufacturing the laminated sheet by laminating a plurality of materials to be laminated containing a heat-fusible material to be laminated by a pressure and heating molding apparatus, a protective material, of which the tensile elastic modulus at a laminating temperature is 50 kgf/mm² or more and the coefficient of linear expansion at 200-300°C is 100 ppm/°C or less, is arranged between the pressure surface of the molding apparatus and the materials to be laminated to perform pressure and heating molding at 200°C or higher and, after cooling, the protective material is peeled from the laminated sheet.

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[JP,2001-310344,A]

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DETAILED DESCRIPTION [JP,2001-310344,A]

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of the laminate manufactured with pressurization hot-forming equipment. It is related with the manufacture approach of the flexible laminate especially used for an electronic electrical machinery and apparatus etc.

[0002]

[Description of the Prior Art] There are a laminate (it expresses the laminate of a heat-curing mold hereafter) on which the metallic foil was stuck by heat-curing mold adhesives, such as thermosetting resin, and a laminate (it expresses the laminate of a thermal melting arrival mold hereafter) stuck by thermal melting arrival mold adhesives, such as thermoplastics, as laminate used for the printed circuit board for electronic electrical machinery and apparatus.

[0003] The manufacture approach of the laminate of a heat-curing mold is studied variously conventionally. An impregnated paper, A resin sinking-in glass fabric etc. and a metallic foil are pressed using a multi-platen press or the vacuum press. Then, on both sides of the approach of carrying out heat curing at an elevated temperature for several hours, and obtaining a rigid laminate, and a roll-like ingredient, it laminates in one pair of heating rollers. Then, the approach of carrying out heat curing at an elevated temperature for several hours, and obtaining a flexible laminate, the approach of using double belting press equipment instead of a heating roller, and carrying out a heat lamination, etc. are enforced. When manufacturing the laminate of these heat-curing mold, it is that pressurization heating molding temperature is 200 degrees C or less in most cases. In whenever [of this level stoving temperature], the thermal stress concerning a laminated ingredient is small, and it is hard to generate a poor appearance, such as Siwa at the time of a heat lamination. In the approach of manufacturing the laminate of these heat-curing mold, there is the approach of carrying out pressurization hot forming on both sides of a protective material between the pressurization side of equipment and a laminated ingredient. When time manufactures the laminate of a thermal melting arrival mold with (JP,60-109835,A and JP,4-89254,A), if pressurization heating is not performed at the temperature more than the glass transition temperature (Tg) of the thermoplastics which constitutes a glue line, thermal melting arrival is not made. On the other hand, since the laminate for electronic electrical machinery and apparatus receives heating at high temperature in process of component mounting, the thermoplastics which constitutes a

glue line is asked for Tg at least 180 degrees C or more. Therefore, for the thermal melting arrival, the heat lamination temperature of 200 degrees C or more is needed. In the lamination in such an elevated temperature, change of the thermal expansion and the heat shrink of a laminated ingredient became large, and the problem of being easy to produce a poor appearance, such as Siwa, was in the laminated layered product.

[0004]

[Problem(s) to be Solved by the Invention] This invention aims at offering a laminate suitable as a flexible substrate ingredient without a poor appearance, such as Siwa produced at the time of a heat lamination, in view of said trouble.

[0005]

[Means for Solving the Problem] When this invention persons arranged and laminated the specific protective material between the pressurization side and the laminated ingredient, it found out that a motion of the direction of a field is controlled since the thermoplastic polyimide after a lamination has a protective material in the outside of copper foil, although it is going to contract, a motion of thermoplastic polyimide was restricted, and Siwa did not occur. It is the manufacture approach of the laminate which comes to stick two or more laminated ingredients containing the laminated ingredient of 1 thermal-melting arrival nature with pressurization hot-forming equipment. Namely, between the pressurization side of this equipment, and a laminated ingredient The protective material whose modulus of elasticity in tension in the temperature of lamination is two or more [50 kgf(s)/mm] and whose coefficient of linear expansion in 200 to 300 degrees C is 100 ppm/degree C or less is arranged. The manufacture approach of the laminate characterized by performing pressurization hot forming 200 degrees C or more, and exfoliating this protective material from a laminate after cooling.

2) The manufacture approach of the laminate given in one characterized by carrying out pressurization heating of said charge of a laminated wood continuously, and coming to stick.

3) The manufacture approach of a laminate given in 1 or 2 which said protective material consists of a polyimide film of non-thermoplasticity, and is characterized by the thickness being 50 micrometers or more.

4) The manufacture approach of a laminate given in any 1 term of 1 thru/or 3 characterized by sticking two or more sorts of laminated ingredients.

5) The manufacture approach of a laminate given in any 1 term of claim 1 characterized by thickness using a metallic foil 50 micrometers or less as a laminated ingredient thru/or claim 4.

6) The manufacture approach of a laminate given in any 1 term of 1 thru/or 5 characterized by using the charge of a binder which contains thermoplastic polyimide 50% of the weight or more as a laminated ingredient.

7) The manufacture approach of a laminate given in any 1 term of 1 thru/or 6 to which pressurization hot-forming equipment is characterized by being a hot calender roll lamination machine or a double belting press machine.

8) The manufacture approach of a laminate given in any 1 term of 1 thru/or 7 characterized by using the long sheet-like object rolled in the shape of a roll as either [at least] a laminated ingredient or a protective material.

9) The manufacture approach of a laminate given in any 1 term of 2 thru/or 7 characterized by repeating and using said protective material.

[0006]

[Embodiment of the Invention] Hereafter, the detail of this invention is explained.

[0007] Although especially the application of the laminate obtained by the manufacture approach of this invention is not limited, it is used mainly as a flexible laminate for electronic electrical and electric equipment. In addition, the laminated ingredient as used in the field of this invention points to the shape of a sheet and the tabular ingredient finally unified as a laminate, and the laminated ingredient of thermal melting arrival nature points to the laminated ingredient which has the function to paste up laminated ingredients by the welding by heating. Moreover, a protective material puts the non-component of a laminate. When taking approaches, such as performing pressurization hot forming multistage, a protective material may be arranged without [which does not contact the pressurization side of pressurization hot-forming equipment] ** or adjoining.

[0008] As a laminated ingredient of thermal melting arrival nature used for this invention, although a thermoplastics film, the adhesion sheet of thermal melting arrival nature, a thermoplastics impregnated paper, thermoplastics sinking-in glass fabrics, etc. are mentioned, as an object for flexible laminates, a thermoplastics film and the adhesion sheet of thermal melting arrival nature are desirable. What has thermal resistance as a thermoplastics film is desirable, for example, moldingses, such as thermoplastic polyimide, thermoplastic polyamidoimide, thermoplastic polyether imide, and thermoplastic polyester imide, are mentioned, and thermoplastic polyimide and thermoplastic polyester imide may be used especially suitably. Use of the adhesion sheet of thermal melting arrival nature with which the adhesion sheet of the thermal melting arrival nature which contains these heat-resistant thermoplastics 50% or more was also preferably used for this invention, and blended thermosetting resin like especially an epoxy resin and acrylic resin etc. is desirable. Moreover, various additives may be blended with the thermal melting arrival nature sheet for improvement in various properties.

[0009] Although especially the configuration of the charge of a heat-resistant binder is not specified, it may have a certain amount of rigidity, and sufficient sufficient insulating property and adhesive property from one layer of adhesives layers. Moreover, in order to acquire the rigidity of the charge of a binder, it is good for the core of an adhesives layer also as a three-tiered structure using the polyimide film of non-thermoplasticity with rigidity.

[0010] Although especially the production approach of the laminated ingredient of thermal melting arrival nature is not specified, when consisting of one layer of adhesives layers, a film can be produced with the belt cast method, an extrusion method, etc. Moreover, the approach of applying an adhesives layer to every [one side] or double-sided coincidence, and when the configuration of the charge of a heat-resistant binder consists of three layers, such as a glue line / core film / glue line, and using the adhesives of a polyimide system especially, it applies with polyamic acid and the approach of subsequently imide-izing and the method of applying and drying fusibility polyimide resin as it is are in both sides of a core film. In addition, the co-extrusion of each resin of a glue line / core film / glue line is carried out, and there is the approach of producing the charge of a heat-resistant binder at once etc.

[0011] Although not limited especially about laminated ingredients other than the laminated ingredient of the ***** aforementioned thermal melting arrival nature for

this inventions, it is desirable to stick two or more sorts of laminated ingredients, two or more sorts of laminated ingredients more preferably chosen from a metallic foil, plastic film, an impregnated paper, resin sinking-in glass fabrics, and a resin sinking-in nonwoven glass fabric especially a metallic foil, and plastic film.

[0012] About a metallic foil, copper foil is desirable and copper foil 50 micrometers or less is more desirable. Especially, since copper foil 35 micrometers or less tends to produce Siwa in case it is limp compared with the copper foil of the thickness beyond it and a heat lamination is carried out, this invention demonstrates remarkable effectiveness about copper foil 35 micrometers or less. Moreover, as a class of copper foil, rolling copper foil, electrolytic copper foil, HTE copper foil, etc. are mentioned, there is especially no limit and adhesives may be applied to these front faces.

[0013] As plastic film, a thermosetting resin film, the adhesion sheet which formed thermosetting resin into B stage, a thermoplastics film, the charge of a binder of thermal melting arrival nature, a non-thermoplastics film, etc. are mentioned. A polyimide film is mentioned as an example of representation of a non-thermoplastics film. Adhesives may be applied to one side or both sides at plastic film if needed, and laminate molding which starts this invention further may be presented with the film by which laminate molding was already carried out.

[0014] About pressurization hot-forming equipment, a laminated ingredient is heated, especially if it is equipment which applies and laminates a pressure, it will not be scrupulous, for example, single action press equipment, multi-platen press equipment, vacuum press equipment, multistage vacuum press equipment, autoclave equipment, a hot calender roll lamination machine, a double belting press machine, etc. are mentioned, and a hot calender roll lamination machine and a double belting press machine may be used preferably among these. If the long sheet-like object especially rolled in the shape of a roll as a laminated ingredient and a protective material is used combining these equipments, continuation manufacture of a laminate will be attained and it will lead to improvement in productivity. About the heating approach, especially if it can heat at predetermined temperature, it will not be scrupulous, and a thermal circuit system, a hot blast heating method, a dielectric heating method, etc. are held. Although whenever [stoving temperature] has desirable 200 degrees C or more, when the application which passes through the solder reflow furnace of 240 degrees C of ambient temperature is presented with a laminate for electronic-parts mounting, in order to use the thermal melting arrival sheet which has Tg according to it, heating of 240 degrees C or more is desirable. Especially if a predetermined pressure can be applied also about a pressurization method, it will not be scrupulous, and an oil hydraulic system, a pneumatic pressure method, the pressure method between gaps, etc. are held, and especially a pressure is not limited.

[0015] The protective material which is an ingredient for protecting from a poor appearance, such as Siwa, in this invention is indispensable. In addition, the approach of carrying out pressurization hot forming on both sides of a protective material between the pressurization side of equipment and a laminated ingredient is indicated by JP,60-109835,A and JP,4-89254,A. All were what manufactures the laminate of a heat-curing genotype, 200 degrees C or less and the case of being low are most, and pressurization heating molding temperature cannot generate a poor appearance, such as Siwa, easily from the first, so does not say that generating of Siwa the purpose of whose is also the

effectiveness of this invention is prevented, and prevents generating of the curvature of a laminate [in / in preventing the blemish on the front face of a metallic foil, and generating of a dent **** / the curing oven after a heat lamination]. Or although a protective material may be used when the problem of smooth lamination being checked with a scarce impregnated paper, a resin sinking-in glass fabric, etc. by smooth nature with a resin rich area ball occurs, it differs from the purpose of the invention in this application greatly.

[0016] If the cause of generating of Siwa is explained in detail, when it laminates copper foil and thermoplastic polyimide with a hot calender roll lamination machine, copper foil and thermoplastic polyimide will be stuck by passing through between the press rolls of a hot calender roll lamination machine, for example. The heat lamination of the thermoplastic polyimide is carried out with copper foil in the condition of generally having been extended more greatly [the direction of a field] than copper foil since the coefficient of linear expansion of thermoplastic polyimide was larger than the coefficient of linear expansion of copper foil although it was in the condition that each laminated ingredient expanded with heat at the time of a lamination, and conversely, at the time of cooling, thermoplastic polyimide is larger than copper foil in the direction of a field, and it is shrunken. For this reason, the made laminate produces Siwa in the direction of a field. Heat is held, since the temperature is higher than Tg of thermoplastic polyimide, thermoplastic polyimide has an ingredient in a flow condition, and immediately after the lamination by which, as for this, a pressure is opened wide is also considered that it is a cause that generating of Siwa cannot be inhibited.

[0017] Therefore, at the time of heating, if a certain amount of hardness is not held, since a protective material cannot bear a role of a protective material, it requires that the modulus of elasticity in tension in lamination temperature should hold two or more [50 kgf(s)/mm]. A crack may occur depending on the pressure laminated as an elastic modulus is less than [50 kgf(s)/mm] two. Moreover, as for the coefficient of linear expansion of a protective material, it is desirable that it is 100 ppm/degree C or less. If coefficient of linear expansion is larger than degree C in 100 ppm /, since the dimension of a protective material will change with the heating-cooling cycles at the time of lamination a lot compared with a laminated ingredient, the bad influence of making the front face of a laminated ingredient producing Siwa is done after lamination.

[0018] Said protective material has effective metallic foils, such as a polyimide film which has the thermal resistance beyond it, copper foil, aluminium foil, and an SUS foil, etc., when the temperature at the time of processing can be borne and it processes [for example,] it at 250 degrees C. Moreover, when using the polyimide film generally marketed, the thickness of the point of controlling the Siwa formation of the laminate after a lamination to a protective material has desirable 75 micrometers or more.

[0019] The temperature of the laminate at the time of exfoliating a protective material has the desirable temperature below the Tg, when using thermoplastics as a laminated ingredient. They are more desirable temperature lower 50 degrees C or more than Tg and still more desirable temperature lower 100 degrees C or more than Tg. When most preferably cooled to a room temperature, it is desirable to exfoliate a protective material from a laminate.

[0020] Said protective material can be repeated and used in this invention. Not to mention installing a delivery and take-up motion of a laminated ingredient before and

after a hot calender roll lamination machine, a protective material is reusable by rolling round the protective material once used by lamination with take-up motion, and installing it in a delivery side again by putting side by side the delivery and take-up motion for protective materials. In case it rolls round, edge location detection equipment and winding location correction equipment may be installed, and the edge of a protective material may be arranged and rolled round with a sufficient precision.

[0021] An example is indicated below and this invention is explained more to a detail.

[0022]

[Example] (Examples 1 and 2) the both sides of the 25-micrometer thermoplastic polyimide film (PIXEO[by Kaneka Co., Ltd.] TP-T) of Tg190 degree C -- 18-micrometer rolling copper foil -- the protective material was further arranged on the both sides, and the heat-resistant flexible laminate was produced on condition that the lamination temperature of 300 degrees C, lamination pressure 50 kgf/cm, and lamination rate 2 m/min using the hot calender roll lamination machine. Detail conditions are shown in Table 1. Consequently, the flexible laminate which does not have the defect of Siwa etc. in an appearance was obtained. In addition, the modulus of elasticity in tension was measured by crosshead speed (speed of testing) 200 mm/min using : autograph [by Shimadzu Corp.] S-100-C based on JIS K713. Coefficient of linear expansion was measured by the programming rate of 10 degrees C / min using : thermal-analysis equipment TMA8140 by Rigaku Corp. based on JIS K7197.

[0023] (Examples 1 and 2 of a comparison) The flexible laminate was produced on condition that Table 1 like the example 1.

[0024] Consequently, Siwa where the vertical reinforcement went into the travelling direction of a lamination occurred.

[0025]

[Table 1]

	実施例 1	実施例 2	比較例 1	比較例 2
保護材料	ポリイミドフィルム*1	銅箔	なし	ポリフェニレンサルファイドフィルム
初期引張弾性率 (kgf/mm ²) at 300℃	1 2 0	6 0 0 0	—	測定不能
線膨張係数 (ppm/℃) at 200-300℃	4 0	2 0	—	測定不能
厚み (μm)	7 5	7 5	—	7 5
リサイクル	可能	可能	—	不可能
外観	シワなし	シワなし	シワあり	保護材料が伸びてしまい作製不可能

* 1 鐘淵化学工業 (株) 製 アピカル

[0026]

[Effect of the Invention] A laminate with a good appearance can be obtained by using the manufacture approach of the laminate by this invention.

CLAIMS

[Claim(s)]

[Claim 1] It is the manufacture approach of the laminate which comes to stick two or more laminated ingredients containing the laminated ingredient of thermal melting arrival nature with pressurization hot-forming equipment. Between the pressurization side of this equipment, and a laminated ingredient The protective material whose modulus of elasticity in tension in the temperature of lamination is two or more [50 kgf(s)/mm] and whose coefficient of linear expansion in 200 to 300 degrees C is 100 ppm/degree C or less is arranged. The manufacture approach of the laminate characterized by performing pressurization hot forming 200 degrees C or more, and exfoliating this protective material from a laminate after cooling.

[Claim 2] The manufacture approach of the laminate according to claim 1 characterized by carrying out pressurization heating of said charge of a laminated wood continuously, and coming to stick.

[Claim 3] The manufacture approach of the laminate according to claim 1 or 2 which said protective material consists of a polyimide film of non-thermoplasticity, and is characterized by the thickness being 50 micrometers or more.

[Claim 4] The manufacture approach of a laminate given in claim 1 characterized by sticking two or more sorts of laminated ingredients thru/or any 1 term of 3.

[Claim 5] The manufacture approach of a laminate given in any 1 term of claim 1 characterized by thickness using a metallic foil 50 micrometers or less as said laminated ingredient thru/or claim 4.

[Claim 6] The manufacture approach of a laminate given in claim 1 characterized by using the charge of a binder which contains thermoplastic polyimide 50% of the weight or more as a laminated ingredient of said thermal melting arrival nature thru/or any 1 term of 5.

[Claim 7] The manufacture approach of a laminate given in any 1 term of claim 1 to which pressurization hot-forming equipment is characterized by being a hot calender roll lamination machine or a double belting press machine thru/or claim 6.

[Claim 8] The manufacture approach of a laminate given in any 1 term of claim 2 characterized by using the long sheet-like object rolled in the shape of a roll as either [at least] a laminated ingredient or a protective material thru/or claim 7.

[Claim 9] The manufacture approach of a laminate given in claim 1 characterized by repeating and using said protective material thru/or any 1 term of 8.